# Ecology and New Building Materials and Products

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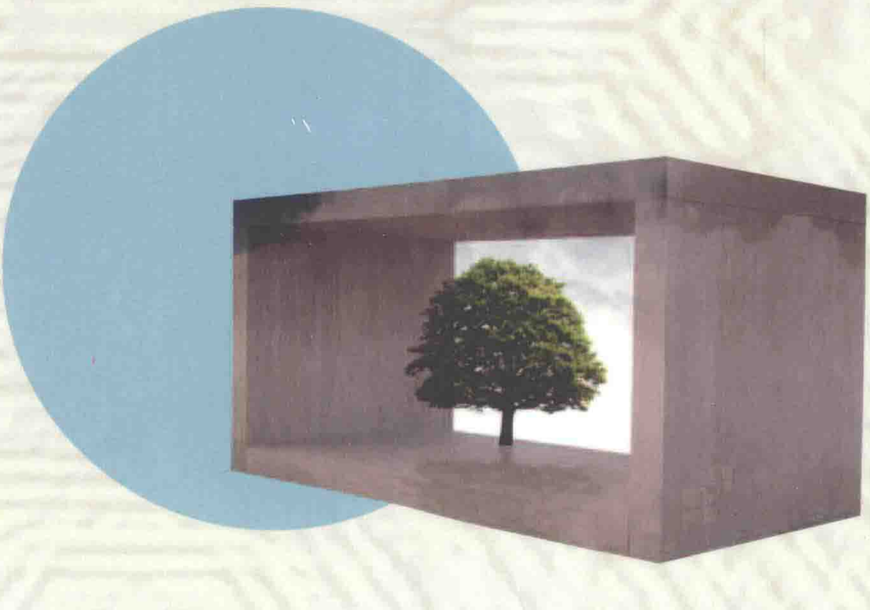

Edited by
Martina Drdlová, Martin Nejedlík
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# Ecology and New Building Materials and Products

Selected, peer reviewed papers from the
18th Conference of Research Institute for
Building Materials Ecology and New Building
Materials and Products
(ICEBMP 2014),
June 3-5, 2014, Černá Hora, Czech Republic

*Edited by*

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Trans Tech Publications Ltd
Churerstrasse 20
CH-8808 Pfaffikon
Switzerland
http://www.ttp.net

Volume 1000 of
*Advanced Materials Research*
*ISSN print 1022-6680*
*ISSN cd 1022-6680*
*ISSN web 1662-8985*

Full text available online at *http://www.scientific.net*

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PO Box 699, May Street
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printed in Germany

# Preface

By establishing the International Conference „Ecology and new building materials and products“ in 1996 an international forum for the exchange of both scientific and practical knowledge was created. One aim of the conference has always been to bring researchers from universities and industrial enterprises together to share their experience.

As in the past, the scope of the conference is focused on problems of the development and application of building materials with emphasis on waste utilization. The conference covers the newest knowledge and progressive trends in the field of ecology and new building materials and products. Both scientific and practical knowledge in the field of civil engineering industry and related topics are presented.

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# CHAPTER 1:

# Binders

*Advanced Materials Research Vol. 1000 (2014) pp 3-6*
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*doi:10.4028/www.scientific.net/AMR.1000.3*

# The influence of sodium sulphite on Portland clinker hydration

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**Keywords:** Portland clinker, sodium sulphite, sulphite-containing AFm

**Abstract.** AFm phases, called also ($Al_2O_3$-$Fe_2O_3$-mono), are a common term for the hydration products with general formula $[Ca_2(Al,Fe)(OH)_6{\cdot}(X)]{\cdot}y\ H_2O$, where X means e.g. $OH^-$, $SO_4^{2-}$, $CO_3^{2-}$. AFm phases are formed when the corresponding phases are present in adequate concentrations in the solution under the room temperature. The incorporation of sulfite anions in the structure of lamellar AFm phase will be shown. The presence of monosulphite in the Portland clinker system was investigated by infrared spectroscopy, XRD and SEM analyses.

## Introduction

Nowadays, the use of waste materials in cement production is a very actual topic. This fact should solve two main problems: large amount of waste and the decrease of financial aspects of production.

The use of waste materials in cement production could cause many undesirable changes in the composition, structure and properties of produced cement. This study aims at the influence of sulphite anions on the Portland clinker hydration. Many studies describe a new phase – sulphite containing AFm phase [1,2]. The results published by some authors complement each other, but only pure sulphite AFm phases were prepared. In this study the phase prepared by real system from Portland clinker was investigated.

For the application of sulfite-containing products in building materials industry, a better understanding of the hydration reactions and of the properties of sulfite-containing hydrates is necessary.

## Experimental

**Materials.** The Portland clinker from Českomoravský cement, a.s. Mokrá cement plant was used in all experiments. The particle size of used clinker was $d_{50}$ = 8.07 µm, $d_{90}$ = 39.30 µm, $d_{99}$ = 70.15 µm (the numbers mean the percent (50 %, 90 % and 99 %) of particles smaller than this value).

The added component used in this study was sodium sulphite p.a. ($Na_2SO_3$) from Lach-ner s.r.o. with 98 % minimum content. The next substance was precipitated calcium sulphate dihydrate pure from Lachema s.r.o.

The experimental samples were prepared by mixing Portland clinker with 5 wt. % sodium sulphite. The water to cement ratio was 0.5. The samples containing 5 wt. % of calcium sulphate were also prepared and used for the comparison of formed hydration products. 28-days-old samples were investigated by the testing methods described below.

**Methods.** The X-ray powder diffraction data were obtained using PANanalytical Empyrean diffractometer with CuK$\alpha$ radiation equipped with a 3D detection system PIXcel3D. The specimens were step scanned from 5° to 90° 2$\theta$ using vertical high-resolution goniometer with the step size of 0.013° 2$\theta$. The anode material was Cu, generator voltage – 40 kV and the tube current was 30 mA.

The samples for FT-IR studies were prepared by mixing with KBr in the ratio of 1:100. The mixture was placed in the pressing form and the pellets were prepared. Infrared spectra of pelletized samples were collected by Nicolet Impact 400 FT-IR instrument.

The structure of 28-days-old hydration products was determined by scanning electron microscopy (SEM) using Field emission electron microscope Jeol JSM-7600F. The elemental composition was determined by energy dispersive X-ray micro-analysis (EDX).

**Results and discussion**

**XRD analysis.** The tricalciumaluminate present in Portland clinker reacts with gypsum while ettringite is formed. Ettringite is formed as the first phase and it is converted to monosulphate if the amount of tricalciumaluminate is sufficient. Ettringite prevents clinker from very fast setting and its formation was measured immediately after mixing with water (Fig.1). Rapid increase of portlandite content with time of hydration and the decrease of tricalciumsilicate content approximately in the same time was observed. The decrease of tricalciumsilicate content can be explained by the hydration and the formation of CSH gel and portlandite.

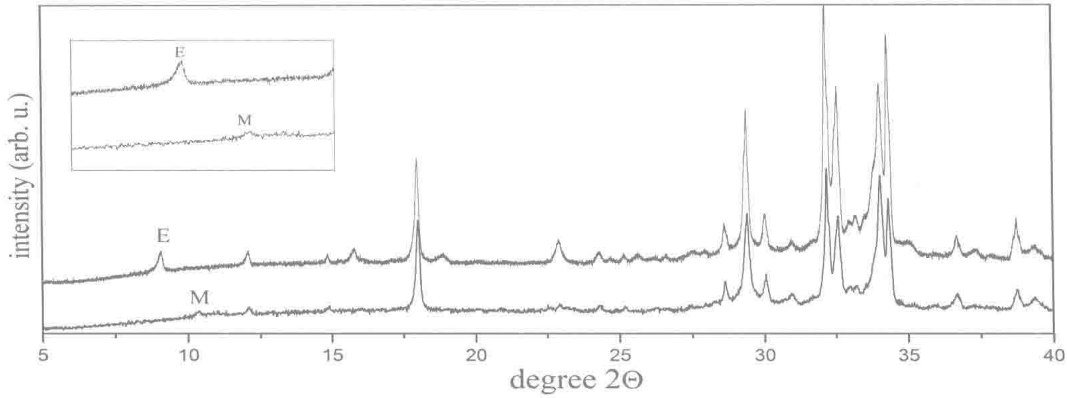


Fig. 1. XRD analyses of Portland clinker with calcium sulphate (top curve) and Portland clinker with sodium sulphite (bottom curve). (E – ettringite, M – monosulphite)

The tricalciumaluminate hydration showed different behavior with the addition of sodium sulphite. XRD analyses didn`t confirm any hydration products similar to ettringite. The tricalciumsilicate hydration started approximately after the second hour of hydration and the amount of portlandite was increased. The new hydration product was formed with the time of hydration. Its general formula is $Ca_4Al_2O_6SO_3 \cdot 11\ H_2O$. The structure of this product is the same as that of monosulphate while the sulphate anions are replaced by sulphite anions. The monosulphite formation is direct without the formation of ettringite and its gradual decomposition. It is the main difference between the hydration of Portland cement and Portland clinker with the addition of sodium sulphite. This statement is based on study [1]. It shows that ettringite isn´t formed by the reaction of tricalciumaluminate with sulphite anions. The hydration product is monosulphite.

**Infrared spectroscopy.** FT-IR spectroscopy is the most common method used for molecular characterization. The presence of sulfite instead of sulphate can be demonstrated clearly using the spectroscopic methods as we can see in Fig. 2. The band at 3643 $cm^{-1}$ is due to $OH^-$ from $Ca(OH)_2$. The broad band centered at 3 400 $cm^{-1}$ is due to symmetric and asymmetric stretching vibrations of O-H adsorbed molecules. The bands at 2359 $cm^{-1}$ and 2338 $cm^{-1}$ mean the presence of carbon dioxide. The band at 1643 $cm^{-1}$ is due to the H-O-H deformation vibration [3]. The band at 1474 $cm^{-1}$ is formed from the reactions of atmospheric $CO_2$ with calcium hydroxide [4]. The $SO_3^{2-}$ vibration was found at 1412 $cm^{-1}$. The very weak band at 1101 $cm^{-1}$ is due to very small amount of sulphate vibration [1]. The band at 953 $cm^{-1}$ is associated with the stretching vibration of $Si\text{-}O\text{-}X^+$ (X = alkaline elements, in our case it is Na). It could explain where sodium was incorporated. The 873 $cm^{-1}$ band is probably caused by the vibration of $CO_3^{2-}$ anion from new carbonates formed and the 827 $cm^{-1}$ band is probably due to the O–Si–O symmetric stretching [5].

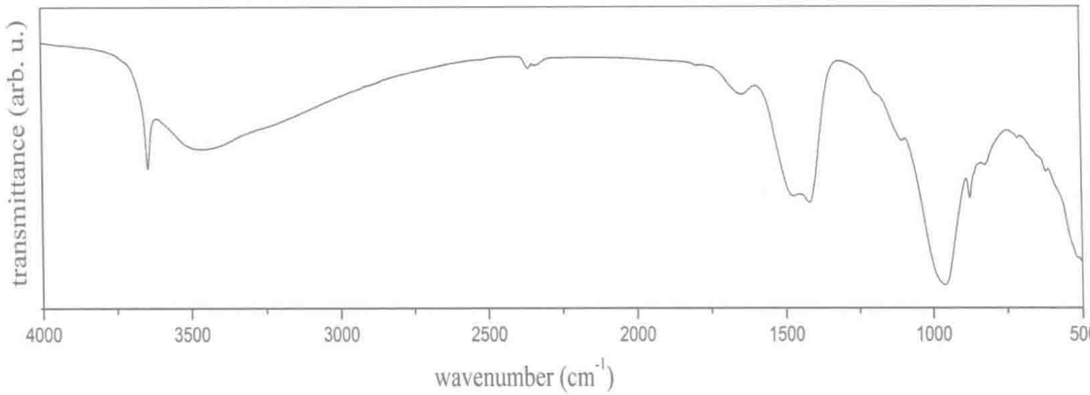


Fig. 2 Transmittance IR spectrum of mixture of Portland clinker with sodium sulphite

**SEM analysis**. The microstructure of hydration products of Portland clinker with the addition of calcium sulphate and sodium sulphite was determined by scanning electron microscopy.

*Portland clinker with calcium sulphate:* Ettringite is formed as a protective layer on the surface of grains. Its main function is preventing Portland clinker from rapid setting. The typical acicular structure of ettringite is shown in Fig. 3. The content of elements in the structure of ettringite is shown in Table 1. The main elements are calcium, aluminum, sulphur, oxygen and hydrogen. Hydrogen cannot be determined by EDX analysis. The characteristic ratio of Al/S in ettringite structure is 2/3 what correspond to obtained data.

*Portland clinker with sodium sulphite:* The XRD analysis identified a new product monosulphite $Ca_4Al_2O_6SO_3 \cdot 11\ H_2O$. Fig. 3 shows the microstructure of this product. Its typical lamellar structure can be observed. This structure is characteristic for a whole group of AFm phases and it is very similar to portlandite structure. The presence of quite big amount of aluminium, sulphur and oxygen is the evidence that the investigated product isn´t portlandite. The atomic ratio of Al/S in the structure of monosulphite is 2/1 what correspond to obtained data in Table 1.

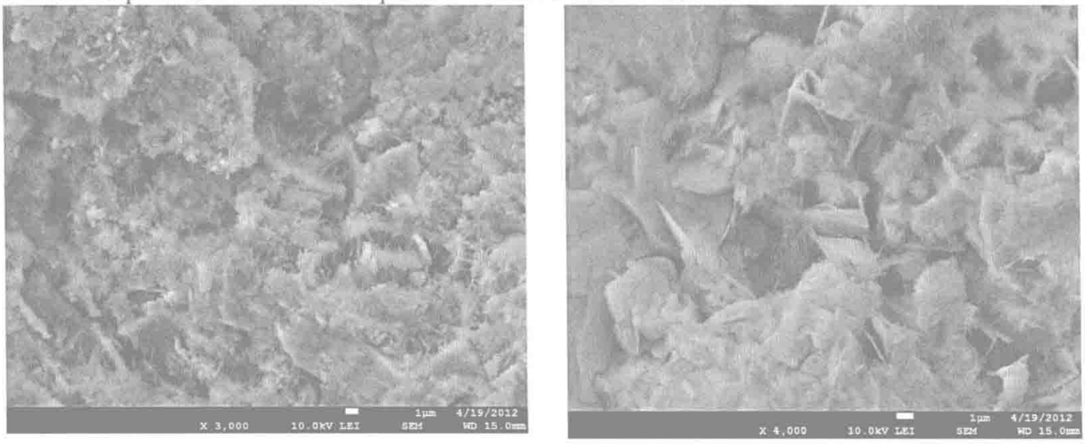


Fig. 3. SEM analysis of hydration products: clinker with calcium sulphate (left) and clinker with sodium sulphite (right).

The elements sodium, magnesium, silicon and potassium are present due to the discontinuity of surface and the big size of interaction volume. In this study the size of interaction volume was 3 μm which is larger than the thickness of analysed layer. The presence of iron can occur due to the substitution by iron instead of aluminium in the structure of AFt or $SO_3$-AFm. $C_4AF$ can be observed too.

Table 1. Elemental composition of hydration products

| | | O | Na | Mg | Al | Si | S | K | Ca | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| **sulphate clinker** | [wt. %] | 48.38 | 0.29 | 0.23 | 1.62 | 8.53 | 2.60 | 2.18 | 34.85 | 1.33 |
| | [at. %] | 68.11 | 0.29 | 0.21 | 1.35 | 6.84 | 1.83 | 1.25 | 19.58 | 0.54 |
| **sulphite clinker** | [wt. %] | 55.87 | 1.05 | 0.18 | 8.12 | 2.19 | 4.16 | 0.21 | 27.10 | 1.12 |
| | [at. %] | 73.44 | 0.98 | 0.16 | 6.33 | 1.64 | 2.73 | 0.11 | 14.22 | 0.42 |

**Summary**

The hydration of Portland clinker in the presence of sulphite leads to the formation of sulphite-containing AFm. The presence of sulphite anions didn´t change the structure of AFm phase, which is typically lamellar. According to XRD analysis the formation of monosulphite phase seemed to be very slow in comparison with the formation of ettringite in Portland cement. The phase similar to ettringite wasn´t formed what agrees with other studies. This process is supposed to have interesting influence on the speed of hydration which could be the object of the next study.

**Acknowledgements**

This work was financially supported by the project "Materials Research Centre at FCH BUT-Sustainability and Development, REG LO1211, with financial support from National Programme for Sustainability I (Ministry of Education, Youth and Sports).

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*Advanced Materials Research Vol. 1000 (2014) pp 7-11*

*doi:10.4028/www.scientific.net/AMR.1000.7*

# Potential application of belite clinker

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**Keywords:** belite clinker, alite-belite blended cement, hydraulic activity

**Abstract.** Blended cements were prepared from belite clinker burned in a model kiln and ordinary industrial alite clinker. The mechanical and physical properties of these blended cements were determined. The difference in the development of hydration heat of belite and alite cements by using calorimetric method was determined also. The results show that strengths of prepared belite cement after 28 days of hydration are equal to those of industrial alite cement. Short time strengths are suitable for blended cements up to 30 % content of belite clinker. These results demonstrate the possibility of separate industrial belite clinker production next to common alite clinker manufactory and production of economically and ecologically advantageous blended Portland cements with suitable technological properties.

## Introduction

The cement production is characterized by processing large volumes of natural raw materials and high energy consumption. Therefore, main efforts of producers are oriented to optimized usage of primary raw material resources, utilization of secondary waste materials and secondary energetic resources and achievement of high quality and durability of cement products.

The research and the production of hydraulically active low-energy cements, especially of those based on high belite content, is again very relevant and for the future of cementitious binders highly prospective.

Belite has in ordinary Portland clinker considerably lower hydraulic activity than alite [1] but it contributes significantly to strength development after 28 days of hydration. This led to efforts to stabilize hydraulically active forms of belite, above all of its high-temperature modifications. One of the ways of stabilization is chemical stabilization by suitable admixtures, usually complemented by extremely fast cooling [2-6]. Newer method of hydraulic activation of belite is utilization of the so called remelting reaction [7, 8], when controlled cooling and addition of admixtures are accompanied by phase transformations connected with release of fluid phase and destruction of $C_2S$ crystals. Such method can be realized only under conditions beyond the possibilities of currently used industrial technologies. The research of the mechanism and kinetics of formation of low-alite up to pure belite clinkers showed that quickly formed belite clinker has (in contrary to original expectations) lower hydraulic activity than longer burned, recrystallized belite clinker [9]. One of the other possible directions is separate alternating production of belite clinker and classic alite clinker and then to manufacture from them a wide range of blended cements with demanded properties.

## Materials and methods

The raw materials used for the preparation of experimental mixture were pure limestone (L1), limestone with increased $SiO_2$ content (L2), clay shale (CS) and iron correction (Fe). The composition of the mixture, which is given in Table 1, was calculated by special software and was based on these chemical parameters: LSF = 80 (lime saturation factor after Lea-Parker), SR = 2.6 (silica ratio), AR = 1.4 (alumina-iron ratio). A certain amount of FGD gypsum was added to the mixture for reducing the alite formation [10], increasing of clinker sulfation and increasing of belite hydraulic activity [11]. The amount of mix, specifically 16 kg, was ground in ball mill to fineness characterized by 13 wt. % of fraction 0.09 mm.